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AUTHOR(S): W. M. Jones and M. G. Bowman

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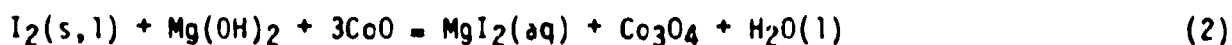
THE USE OF OXIDES IN THERMOCHEMICAL WATER-SPLITTING CYCLES
FOR SOLAR HEAT SOURCES. COBALT OXIDES

W. M. Jones and M. G. Bowman

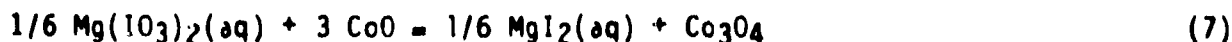
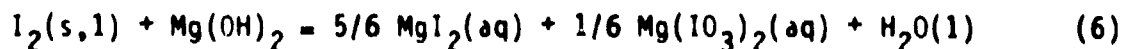
University of California, Los Alamos National Laboratory
Post Office Box 1663, Los Alamos, New Mexico 87545, U.S.A.

ABSTRACT

The concept of utilizing oxide decompositions in advanced thermochemical hydrogen cycles for solar heat sources is introduced. It has particular interest in allowing direct transmission of energy to the process through an "air window". A cycle for the Co_3O_4 -CoO pair would be, schematically:



Reaction (2) should give a high concentration of MgI_2 that would be favorable for (3). The solutions would also contain iodine dissolved as polyiodide, partly offsetting this advantage. Preliminary results indicate that reaction (2) is slow at 150°C . It is surmised that the mechanism of (2) consists of the iodine disproportionation reaction (6), followed by reaction (7).



Other workers have found (6) to be relatively fast and with a good yield at 150°C . We have found reaction (7) to be sufficiently slow at 150°C to account for the slowness of (2). The yield of (7) was found to be proportional to the square root of the time, which suggests that iodate must diffuse through an adherent, accumulating Co_3O_4 layer. Since (7) is much faster when $\text{Mg}(\text{IO}_3)_2$ is replaced by KIO_3 , the magnesium ion may catalyze formation of an adherent Co_3O_4 spinel layer or enter into the structure of the layer. The reactivity of CoO in the KIO_3 analog of (7) is greatly decreased by exposure to high temperature.

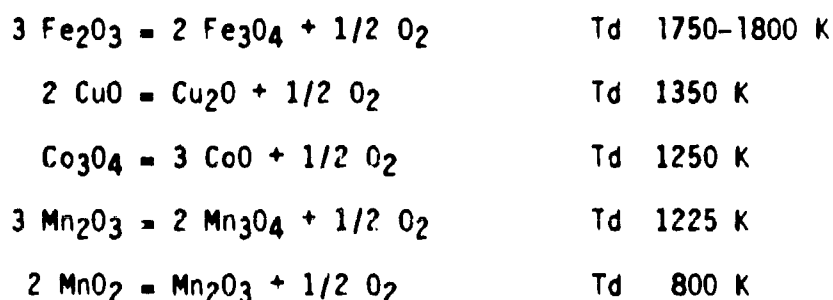
KEYWORDS

Oxides in solar water splitting; cobalt oxides; iodate oxidation of cobalt monoxide.

INTRODUCTION

In addition to solid sulfate cycles as advanced alternatives to sulfuric acid cycles, it is apparent that cycles based on solid oxide decomposition as the high temperature step may offer unique advantages for coupling with a solar furnace, since the oxide can be heated and decomposed in air at temperatures where the oxygen dissociation pressure exceeds the pressure of oxygen in the atmosphere. Thus the oxide could be heated directly by solar radiation entering through an "air window" and the difficult problem of transmitting heat to the process, either through a container wall or a quartz window, might be greatly simplified. The key to practicality for such cycles will be determined by the chemistry of the low temperature reactions required to form the oxide plus an intermediate that can evolve hydrogen as a product in an additional sequence of reactions. Since the decomposition of an oxide exhibits a relatively low entropy change (in comparison to sulfate decomposition) one might expect that the low temperature reactions will be reasonably complex and will probably require solution chemistry for separating the oxide from other products. However, it is quite possible that the advantages of oxide cycles for solar heat may overshadow the disadvantages of the solution chemistry.

At Los Alamos, studies have been initiated to determine practical conditions for the low temperature steps in oxide cycles. Oxide decomposition reactions are also being evaluated in rotary kiln and fluidized bed systems. Specific oxides being considered for a range of decomposition temperatures are:

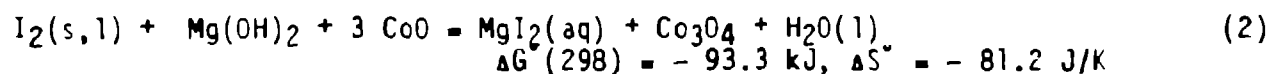


Our initial study is on the Co_3O_4 - CoO pair. It should be emphasized that conditions for the low temperature reactions must still be determined and demonstrated. The possible advantages, however, appear to offer sufficient justification for significant effort, not only at Los Alamos but also in other laboratories.

APPLICATION OF THE Co_3O_4 - CoO PAIR

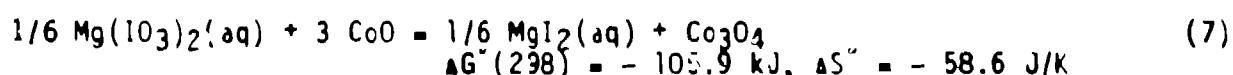
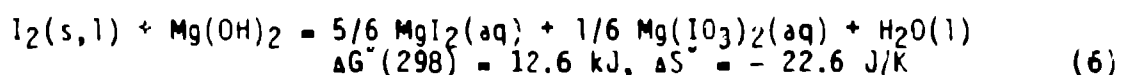
Several thermodynamic studies (JANAF Tables, 1974; U.S. National Bureau of Standards, 1968-1973) indicate the feasibility of decomposing Co_3O_4 to CoO and oxygen at high temperatures. A cycle based on this reaction, with lower temperature reactions represented schematically, would be:





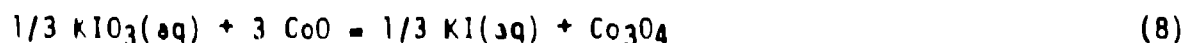
The complication of iodine dissolved as polyiodide is ignored. Some experimental results pertaining to reaction (2) are reported here. Weighed reactants of (2), in stoichiometric proportions (ca. 5 mmol CoO) or with a small excess of I_2 , were placed with about 3 ml H_2O in reaction vessels, which were then flushed with nitrogen, closed, and immersed in baths. Reactants were magnetically stirred during the reaction. Teflon-capped glass Reacti-Vials (5 ml) were used at 78° and 93°C. Most of the experiments were run in a Teflon Parr bomb immersed in a 150°C oil bath. Reaction times were from one to twenty hours. The final solid, or part of it, was freed from I_2 with solvents, washed with water and alcohol, and dried in air or a vacuum. The x-ray powder diffraction patterns showed CoO and $\text{Mg}(\text{OH})_2$ but not Co_3O_4 . Probably not more than 10% of the CoO reacted according to (2).

It seemed likely that a mechanism for (2) would involve disproportionation of I_2 in the presence of $\text{Mg}(\text{OH})_2$, followed by oxidation of CoO by iodate.



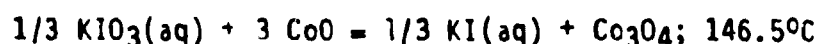
Reaction (6) is not very favorable at 298 K and, making questionable use of the above ΔS° involving ionic entropies at 298 K, might be expected to be less favorable at higher temperature. However, reaction (6) has been studied at 150°C in the context of thermochemical hydrogen by Mason, Farr and Bowman (1980) at Los Alamos and by Japanese workers (Kumagai and others, 1980); appreciable disproportionation was obtained in a few minutes, at least with excess I_2 (Thomas, Pence, and Hasty, 1980). It was also apparent in the present work on the overall reaction (2) that reaction (6) had occurred to some extent, both from the color of the I_3^- ion formed and in one 150°C run from measurement of the iodide ion concentration with a specific ion electrode at the end of the run and at room temperature. In work on (6) at 24°C (I^-), corrected for (I_3^-), was about as predicted. Higher (I^-) was observed after the 150°C run.

Reaction (7) was therefore studied as a potential source of the slowness of reaction (2). In the first experiments KIO_3 rather than $\text{Mg}(\text{IO}_3)_2$ was



used. The reaction yield, limited by the CoO present, was obtained by iodimetric determination of the final iodate. In a 15 h blank run 99.5% of the initial iodate was recovered. The results given in Table 1 show that reaction (8) is reasonably fast, except for Runs 3 and 5. The CoO for Runs 1, 2, 4, and 6 of Table 1 was the same as had been used in the work on reaction (2). The CoO for Run 7 (and for the run of Table 2) was from a second preparation by the same method.

TABLE 1 Reaction



Run	Time, hour	Initial Composition CoO/KIO ₃ /H ₂ O CoO, millimoles	Product x-ray	Fractional Yield
1 ¹	15.3	1/0.1270/69.2 2.38	Co ₃ O ₄	0.77
2	19.3	1/0.1058/65.5 3.33	Co ₃ O ₄	0.85
3	1.0	1/0.1195/49.7 3.33	CoO	—
	19.3	"	CoO	0.05
4	3.5	1/0.1233/61.2 5.37	Co ₃ O ₄	0.85
5 ²	19.7	1/0.1233/62.4 5.28	CoO	<0.10
6	0.75	1/0.1236/61.5 5.36	Co ₃ O ₄	0.86
7 ³	0.75	1/0.1239/30.6 5.37	Co ₃ O ₄ , CoO	0.55

1 Run 1 also had 0.30 millimoles Mg(OH)₂.

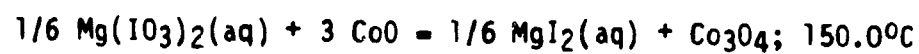
2 Yield estimated from nonappearance of Co₃O₄ in x-ray.

3 New preparation of CoO used.

Except for Runs 3 and 5, the CoO was prepared by thermal decomposition of CoCO₃ in a vacuum system at 300°–400°C with a final 10 h evacuation (10⁻⁵ torr) at 500°–550°C; the particle size was 1 μm or less. The CoO used in Run 3 had been made by oxidizing some of this CoO in air to Co₃O₄ and decomposing the latter in a vacuum system at 870°C for 5 h. The CoO used in Run 5 was made by C. L. Peterson by passing fine Co₃O₄ powder through a laboratory-size rotating kiln in an atmosphere of argon. The residence time in the 1010°C hot zone was about 1 min. Formation of CoO at high temperatures clearly reduces its reactivity. All of these materials had the x-ray powder diffraction pattern of CoO.

Next, reaction (7) itself was studied at 150°C using Mg(IO₃)₂·4H₂O dissolved in H₂O. The MgI₂ concentration was determined with an iodide specific ion electrode after quenching the reactor to room temperature. The calibration solutions were made by dilutions of a solution 0.793 M in MgI₂ and 0.1629 M in Mg(ClO₄)₂ (kept under nitrogen). The perchlorate served to simulate the contribution to the ionic strength of the iodate formed with iodide in (6). The reaction slurries were close to pH7 at room temperature. The results of the single run made are shown in Table 2 and Fig. 1. The reaction rates are much slower

TABLE 2. Reaction



$$\text{CoO}/\text{Mg}(\text{IO}_3)_2/\text{H}_2\text{O} = 1.00/0.0628/38.4$$

$$(\text{CoO}) = 5.29 \text{ millimoles}$$

time, hour	Molarity (MgI_2) $\times 10^3$	Fractional Yield, MgI_2
6.2	1.29	0.0161
22.6	2.43	0.0303
47.0	3.42	0.0427
69.8	4.08	0.0509

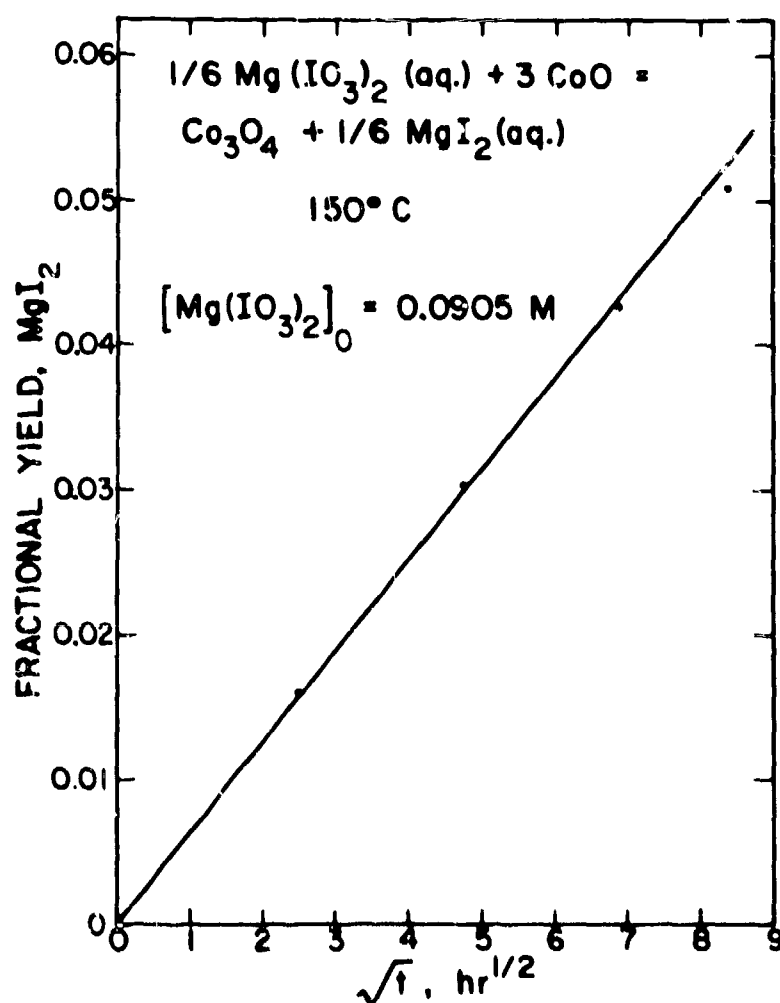


Fig. 1. Fractional reaction yield versus time.

After the analysis at 6.2 h, the speed of the magnetic stirrer was increased by about a factor of three with no effect. Between 47.0 and 69.8 h, the reaction

adherent Co_3O_4 spinel layer may be catalyzed by magnesium ion, itself a former of spinels, or the magnesium may be incorporated into the structure. The small extent of reaction is sufficient to explain the presence only of CoO in the x-ray diffraction pattern of the solid product.

CONCLUSIONS AND FUTURE WORK

The observed slowness of the $\text{Mg}(\text{IO}_3)_2 - \text{CoO}$ reaction (7) is sufficient to explain the slowness of the overall reaction (2). The effort should be on reaction (7), which is much simpler to study than the composite reaction (2). It might also be desirable in a process to conduct (6) and (7) separately. It should be determined whether magnesium is present in the product layer, say as a magnesium-cobalt spinel, or whether the ion acts in some other way, say as a catalyst for formation of a Co_3O_4 spinel adhering to CoO . Investigation should be made of the effects of varying temperature, solution concentrations (especially of Mg^{2+}), and pH (especially in increasing the pH toward a value of roughly 9 characteristic of (2)). The effort appears to be justified by the high magnesium iodide-polyiodide concentrations that should be provided by (2) for reaction (3).

Means for increasing the reactivity of CoO formed at high temperature must also be investigated. Treatment by steam, etching by aqueous CO_2 or other solutions, etc. can be tried.

ACKNOWLEDGEMENTS

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